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Silicone polymer, paste-like composition and water-in-oil type cosmetic composition comprising the same.

A silicone polymer a paste-like silicone composition prepared by kneading the silicone polymer and a silicone oil under a shearing force, and a water-in-oil type cosmetic composition comprising the paste-like silicone composition as an oil phase component are disclosed. The silicone polymer is prepared by the addition polymerization of components comprising an organohydrogeneolysiloxane $R^1_aR^2_bH_cSiO_{(4-a-b-c)/2}$ (1) or $R^1_iH_2SiO_{(4-a-b-c)/2}$ (2) and a polyoxyalkylene $C_mH_{2m-1}O(C_2H_kO)_k(C_3H_kO)_kC_mH_{2m-1}$ (A) or an organopolysiloxane $R^1_iR^1_aSiO_{(4-a-b-c)/2}$ (B), the components including (1) or (A) as an essential component. The silicone polymer can swell in silicone oils and function as a viscosity increasing agent for silicone oils.

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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a silicone polymer, and, more particularly, to a silicone polymer swelling in silicone oil, a paste-like silicone composition comprised of said silicone polymer which is a stable and homogeneous water-in-oil type, and a cosmetic composition comprising said paste-like silicone composition.

Description of the Background Art

Silicone oils are used as a base oil for a number of compositions in a wide variety of fields, including medical products, cosmetics, and the like, because of their safety. In recent years, low viscosity silicone oils, particularly those having viscosities of 100 cS or lower, are attracting the attention due to their superior spreadability, excellent freshness, and high safety. Their applications to various compositions are under study

A large amount of a viscosity-increasing agent must be added for the preparation of a paste-like or greasy silicone composition using such a low viscosity silicone oil as a base oil. The addition of a large amount of a viscosity-increasing agent, however, makes it difficult to obtain a smooth and homogeneous composition and produces a composition with a poor stability due to separation or issue of the low viscosity silicone oil from the composition.

In order to avoid this problem, many types of viscosity increasing agents to be used for low viscosity silicone oils have been proposed, including organic materials, e.g., fatty acid esters of dextrin (Japanese Patent Laid-open (ko-kai) Nos. 121764/1987, 143970/1987, 143971/1987, and 159489/1988), fatty acid esters of sucrose (Japanese Patent Laid-open (ko-kai) No. 235366/1988), trimethyl-silylated polyvinyl alcohols or trimethyl-silylated polysaccharides (Japanese Patent Laid-open (ko-kai) No. 240335/1987), cellulose ethers containing fatty acid ester groups (Japanese Patent Laid-open (ko-kai) No. 260955/1988); and inorganic materials, e.g., montmorillonite clays (Japanese Patent Laid-open (ko-kai) Nos. 45656/1987, 54759 1987, and 72779 1988). The use of these organic or inorganic materials as viscosity increasing agents, however, entails a problem of reducing the inherent characteristics of low viscosity silicone oils, such as expelient froshness and high spreadability.

Therefore a method of producing a homogeneous paste-like composition by treating a specific type of silicone polymer as a viscosity increasing agent and a low viscosity silicone oil under a sharing force was recently proposed (Japanese Patent Laid-open (ko-kai) No. 43283/1990). This method, however, involves a problem in that the composition produced cannot homogeneously disperse water therein when water is added to it oven though it provides an excellent viscosity increasing effect. The use of a surfactant can be considered to ensure homogeneous dispersion of water which is an essential component in many medical or cosmetic compositions. In this case, however, it is difficult to effect stable and homogeneous dispersion of water into silicone cits. In addition, the use of surfactants is undesirable because many surfactants are irritative to the skin.

A first object of the present invention is therefore to provide a novel silicone polymer which is capable of converting a low viscosity silicone oil into a paste-like or greatly composition.

A second object of the present invention is to provide a novel paste-like silicone composition which is capable of discersing water stably and homogeneously without using a surfactant.

A third object of thu prosont invention is to provide a water-in-oil type cosmetic composition which imparting a frosh sonsation upon use without stickiness and stable for a long period of time, and a water-in-oil type cosmetic composition having a superior water repellency and a capability of excellently retaining the make-up without running, both prepared by incorporating a low viscosity silicone oil in the oil phase in a stable manner.

The present inventors have conducted extensive studies in order to develop a silicone polymer which can produce a homogeneous paste-like composition swelling in silicone oil and capable of dispersing water. As a result, the present inventors have found that a polymer swelling in a silicone oil can be obtained by the addition polymerization of a mixture of an organohydrogenpolysiloxane having a polyoxyalkylene group in its molecule and an organopolysiloxane containing an aliphabic unsaturated group in its molecule, or a mixture of an organohydrogenpolysiloxane and a polyoxyalkylene containing an aliphatic unsaturated group (C_mH_{2m-1} group) in its molecule, and that this polymer can act as a viscosity increasing agent for silicone oils and if kneaded under a shearing force together with a silicone oil, can produce a paste-like silicone composition in which water is homogeneously and stably dispersed.

The present inventors have further found that if said mixture is subjected to the addition polymerization in the presence of a silicone oil having a viscosity of 100 cS or lower at 25 °C and/or a polyhydric alcohol, the resulting polymer exhibits even higher swellability in the silicone oil and that, if kneaded under a shearing force together with a silicone oil, this polymer permits water to more stably and homogeneously disperse into a paste-like silicone composition.

The present inventors further undertaken researches concerning the application of the above paste-like silicone composition to cosmetics.

SUMMARY OF THE INVENTION

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Accordingly, an object of this invention is to provide a silicone polymer prepared by the addition polymerization of the following components (I) and (II):

(I) an organohydrogenpolysiloxane represented by the following formula (1),

$$R_a^1R_b^2H_cSiO_{(4-a-b-c)/2}$$
 (1)

wherein R¹ represents a substituted or unsubstituted alkyl, aryl, or aralkyl group having carbon atoms of 1-18, or a halogenated hydrocarbon group; R² represents a group,

wherein R^3 is a hydrogen, a saturated aliphatic hydrocarbon group having 1-10 carbon atoms, or a group -(CO)-R⁵ (wherein R⁵ is a saturated aliphatic hydrocarbon group having 1-5 carbon atoms), d is an integer of 2-200, and e is an integer of 0-200, provided that d + e is 3-200, and n is 2-6; a is a value satisfying inequality 1.0 \leq a \leq 2.5; b is a value satisfying inequality 0.001 \leq b \leq 1.0; and c is a value satisfying inequality 0.001 \leq c \leq 1.0; or an organohydrogenpolysiloxane represented by the following formula (2)

$$R^{1}_{i}H_{g}S_{i}O_{4-1-g+2}$$
 (2)

wherein R' is the same as defined in formula (1), f is a value satisfying inequality $1.0 \le f \le 3.0$, and g is a value satisfying inequality $0.001 \le g \le 1.5$; or a mixture of said organohydrogenpolysiloxanes of formulas (1) and (2) and

(II) a polyoxyalkylene represented by the following formula (A).

$$C_mH_{2m-1}O(C_2H_4O)_n(C_3H_6O).C_mH_{2m-1}$$
 (A)

wherein his an integer of 2-200, i is an integer of 0-200, provided that hill it is 3-200, and m is 2-6, or an organopolysiloxane represented by the following formula (B)

wherein R' is the same as defined in formula (1), R' is a monovalent hydrocarbon group having an alignatic unsaturated bond at the terminal thereof and containing 2-10 carbon atoms, j is a value satisfying inequality 1.0 $\leq j \leq$ 3.0, and k is a value satisfying inequality 0.001 \leq k \leq 1.5, or a mixture of the polyoxyalkylene of formula (A) and the organopolysiloxane of formula (B), wherein at least one organopydrogenpolysiloxane of formula (1) or at least one polyoxyalkylene of formula (A) is contained as an essential component of the addition polymenzation (herein referred to as the first invention).

Another object of the present invention is to provide a silicone polymer which is prepared by additionso polymerizing 100 parts by weight of the components defined in said first invention in the presence of 3-200 parts by weight of a low viscosity silicone oil having a viscosity of 100 cS or lower at 25 °C or a polyhydric alcohol, or both (herein referred to as the second invention).

Still another object of the present invention is to provide a paste-like silicone composition which can disperse water and is prepared by kneading 100 parts by weight of said silicone polymer and 10-1,000 parts by weight of a silicone oil under a shearing force (herein referred to as the third invention).

A further object of the present invention is to provide a water-in-oil type cosmetic composition comprising said paste-like silicone composition as an oil phase component and at least one water phase component (herein referred to as the fourth invention)

In a preferred embodiment of the fourth invention, said water-in-oil type cosmetic composition comprises (i) said paste-like silicone composition and (ii) silicic acid anhydride or hydrophobic silica, or both, as oil phase components, and at least one water phase component (herein referred to as the fifth invention).

In another preferred embodiment of the fourth invention, said water-in-oil type cosmetic composition comprises said paste-like silicone composition as an oil phase component and one or more components selected from the group consisting of saccharides, sugar alcohols, and inorganic salts, as water phase components (herein referred to as the sixth invention)

A further object of the present invention is to provide a water-in-oil type emulsion cosmetic composition comprising said paste-like silicone composition as an oil phase component, at least one water phase component, and a polyoxyalkylene-modified organopolysiloxane type surfactant (herein referred to as the seventh invention).

A still further object of the present invention is to provide a water-in-oil type cosmetic composition comprising said paste-like silicone composition as an oil phase component, at least one water phase component, and a cosmetic powder (herein referred to as the eighth invention).

Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The silicone polymer of the first invention is prepared by the addition polymerization of either an organohydrogenpolysiloxane (1) or (2) or both and either a compound (A) or (B) or both having an aliphatic unsaturated group. It is essential that either the organohydrogenpolysiloxane or the compound having an auphatic unsaturated group contain a polyoxyalkylene group. Therefore, the following combinations of either the organohydrogenpolysiloxane (1) or (2) or both and either the compound (A) or (B) or both having an 1 25 aliphatic unsaturated group are possible.

- (a) The compination of organohydrogenpolysiloxane of formula (1) and organopolysiloxane of formula
- (b) The combination of organohydrogenpolysitoxane of formula (2) and polyoxyalkylene of formula (A).
- (c) The combination of organopydrogenpolysiloxane of formula (1) and polyoxyalkylene of formula (A). The combination (a) is first illustrated in detail.

In formula (1) R'aR'aHcSiO(4-a-b-cyz, which represents organohydrogenpolysiloxane containing a polyoxyalxylene group, R1 is a substituted or unsubstituted alkyl, aryl, or aralkyl group having carbon atoms of 1-18, or a halogenated hydrocarbon group. Specifically, R is selected from alkyl groups, e.g., methyl, ethyl, propyr, butyr, etc., aryl groups, e.g., phenyl, tolyl, etc., aralkyl groups, e.g., benzyl, phenetyl, etc.; and 35 hydrogenated hydrocarbon groups with one or more hydrogen atoms of these alkyl, aryl, or aralkyl groups substituted by halogon atoms, e.g., chloromethyl, trifluoroprocyl, etc. Whon a mixture of organohydrogenpolysildxanes is used different organohydrogenpolysildxane may contain different R1s. R2 represents a polypxya/kylene group of the following formula (3),

42 - C. H2-O(C; H4 O)2(C+H4 O)4R3

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wherein Rriis a hydrogen, a saturated aliphatic hydrocarbon group having 1-10 carbon atoms, e.g., methyl, ethyl, propy', butyl, pentyl, hexyl, heptyl, octyl, etc., or a group -(CO)-R5 (wherein R5 is a saturated aliphatic hydrocarbon group having 1-5 carbon atoms), d is an integer of 2-200, e is an integer of 0-200, provided 45 that d + σ is 3-200, and n is 2-8. The ratio d/e is desirably 1 or more in order to ensure good dispersion of water in the paste-like silicone composition prepared by kneading the obtained polymer and a silicone oil under a shearing force

If the value a in formula (1) is less than 1.0, the obtained polymer cannot sufficiently swell in silicone oils, if greater than 2.5, the paste-like silicone composition prepared by kneading the obtained polymer and so a silicone oil under a shearing force cannot well disperse water therein. Therefore, a should be a value satisfying inequality 1.0 S a S 2.5, and preferably a value of 1.0-2.0. If the value b is less than 0.001, the paste-like silicone composition prepared by kneading the obtained polymer and a silicone oil under a shearing force cannot well disperse water therein, if greater than 1.0, the obtained polymer cannot sufficiently swell in silicone oils. Thus, b should be a value satisfying inequality 0.001 ≤ b ≤ 1.0, and 55 preferably a value of 0.005-1.0. The value of cless than 0.001 makes the formation of the three dimensional structure in the polymer obtained by the addition polymerization difficult, impairing the viscosity increasing capability of the polymer. If the value c is greater than 1.0, on the other hand, the cross-linking density of the three dimensional structure formed by the addition polymenzation becomes too high for the polymer to

retain silicone oils in a stable manner. Therefore, c should be a value satisfying inequality 0.001 ≤ c ≤ 1.0, and preferably a value of 0.005-1.0.

The other component which is combined with the organohydrogenpolysiloxane of formula (1) is organopolysiloxane of the following formula (B),

$$R^{1}_{i}R^{4}_{k}SiO_{(4-j-k)/2}$$
 (B)

wherein R' is the same as defined in formula (1), R* is a monovalent hydrocarbon group having an aliphatic unsaturated group, e.g., vinyl group, allyl group, etc., at the terminal thereof and containing 2-10 carbon atoms. If j in formula (B) is less than 1.0, the cross-linking density of the three dimensional structure formed by the addition polymerization becomes too high for the polymer to retain silicone oils in a stable manner; if it is greater than 3, the formation of the three dimensional structure in the polymer obtained by the addition polymerization is insufficient, resulting in the polymer with a poor viscosity increasing capability. Therefore, j should be a value satisfying inequality $1.0 \le j \le 3.0$, and preferably a value of 1.0-2.5. Regarding the value k, if this value is less than 0.001, the formation of the three dimensional structure in the target polymer obtained by the addition polymerization becomes difficult, resulting in the polymer with a poor viscosity increasing capability; if greater than 1.5, on the other hand, the cross-linking density of the three dimensional structure in the target polymer formed by the addition polymerization becomes too high for the polymer to retain silicone oils in a stable manner. Therefore, k should be a value satisfying inequality 0.001 $\le k \le 1.5$, and preferably a value of 0.005-1.0.

The mixture of organohydrogenpolysiloxane of formula (1) and organopolysiloxane of formula (B) is hereinafter referred to as Mixture-I.

Illustrating the above combination (b), the combination of organohydrogenpolysiloxane of formula (2) and polyoxyalkylene of formula (A), in organohydrogenpolysiloxane of formula (2),

R is the same as defined in formula (1), f is a value satisfying inequality $1.0 \le f \le 3.0$, and g is a value satisfying inequality $0.001 \le g \le 1.5$. If f is less than 1.0, the obtained polymer cannot sufficiently swell in stiticono oits; if greater than 3.0, on the other hand, the formation of the three dimensional structure in the polymer obtained by the addition polymerization becomes difficult, and a only a polymer with a poor viscosity increasing capability is produced. Therefore, f should be a value satisfying inequality $1.0 \le f \le 3.0$, and preferably a value of 1.0-2.5. The value of g less than 0.001 makes the formation of the three dimensional structure in the polymer obtained by the addition polymerization difficult, impairing the viscosity increasing capability of the polymer. The value of g greater than 1.5, on the other hand, makes the crosslinking density of the three dimensional structure formed by the addition polymerization too high for the polymer to retain silicone oils in a stable manner. Therefore, g should be a value satisfying inequality 0.001 $1.0 \le 1.0 \le 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 = 1.0 =$

In polyoxyalkylenes of the following formula (A),

$$C_mH_{2m-1}O(C_2H_6O)_n(C_3H_6O)_nC_mH_{2+m1}$$
 (A)

his an integer of 2-200, and preferably 5-100; and it is an integer of 0-200, and preferably 0-100. The ratio his preferably 1 or more and mis 2-6, and preferably 3-6, in order to ensure good dispersion of water in the resulting polymer.

The mixture of organohydrogenpolysiloxane of formula (2) and polyoxyalkylene of formula (A) is hereinafter referred to as Mixture-II.

For combination (c), the combination of the abovementioned organohydrogenpolysiloxane of formula (1) and polyoxyaixylene of formula (A) can be given as an example. The mixture of organohydrogenpolysiloxane of formula (1) and polyoxyalkylene of formula (A) is hereinafter referred to as Mixture-III.

The silicone polymer of the second invention can be obtained by the addition polymerization of Mixture-II. Mixture-III or Mixture-III in the presence of a low viscosity silicone oil having a viscosity of 100 cS or smaller at 25°C or a polyhydric alcohol, or both. Given as examples of silicone oils having a viscosity of 100 cS or smaller at 25°C are linear or branched methylpolysiloxane, methylphenylpolysiloxane, ethylpolysiloxane, ethylphenylpolysiloxane, cyclic dimethylpolysiloxane, e.g., octamethylcyclototrasiloxane, decamethylcyclopentasiloxane, etc; and the like. The viscosity of these silicone oils is not specifically limited so long as it is 100 cS or lower, preferably 50 cS or lower, at 25°C. These silicone oils can be used either singly or in mixture.

Polyhydric alcohols which can be used for the above addition polymerization include ethylene glycol, 1,3-butylene glycol, propylene glycol, dipropylene glycol, glycerin, diglycerin, and the like. They can be used singly or two or more of them can be used in combination.

In the second invention, in which the addition polymerization of Mixture-II, Mixture-III, or Mixture-III is carried out in the presence of a low viscosity silicone oil having a viscosity of 100 cS or lower at 25 °C or a polyhydric alcohol, or both, the amount of the low viscosity silicone oil and polyhydric alcohol used is 3-200 parts by weight for 100 parts by weight of Mixture-I, -II, or -III. If this amount is less than 3 parts by weight, sufficient effects intended by the present invention cannot be obtained; if greater than 200 parts by weight, the addition polymerization reaction is inhibited, resulting in a poor conversion and producing a polymer product with an insufficient viscosity increasing effect.

In the above addition polymerization, the presence of a low viscosity silicone oil or a polyhydric alcohol results in a silicone polymer containing such a low viscosity silicone oil or a polyhydric alcohol.

In the addition polymerization in the first and second inventions, said Mixture-I, -II, or -III is reacted in the presence of a known platinum catalyst, e.g., chloroplatinic acid, alcohol-modified chloroplatinic acid, or a chloroplatinic acid-vinylsiloxane complex, or in the presence of a rhodium catalyst, at room temperature or with heating at 50-150 °C.

An organic solvent may optionally be used in the reaction. Organic solvents which can be used include alignatic alcohols, e.g., methanol, ethanol, 2-propanol, butanol, etc., aromatic hydrocarbons, e.g., benzene, toluene, xylene, etc., aliphatic or alicyclic hydrocarbons, e.g., n-pentane, n-hexane, cyclohexane, etc., halogenated hydrocarbons, e.g., dichloromethane, chloroform, carbon tetrachloride, trichloroethane, trichloroethylene, fluorochloro hydrocarbons, etc., and the like. Of these, ethanol is preferable taking into consideration the fact that the resulting silicone polymers are applied to medical products and cosmetics.

The paste-like, homogeneous silicone composition, which is the subject of the third invention, can be prepared by mixing 100 parts by weight of the silicone polymer of the first or the second invention and 10-1,000 parts by weight, preferably 20-500 parts by weight, of a silicone oil and kneading the mixture under a shearing force. This paste-like silicone composition can disporse powders and pigments having specific gravities different from that of silicone oils, and can hold them therein in a stable manner without precipitating them. Owing to this characteristic, the composition is useful as a base material for creams, cakes, and the like used in cosmetics and quasi-medical products.

Silicone oils used for the preparation of the paste-like silicone composition may be either linear or branched, and include methylpolysiloxane, methylphenylpolysiloxane, ethylphenylpolysiloxane, ethylphenylpolysiloxane, ethylphenylpolysiloxane, e.g., octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, etc.; and the like. They may be used either singly or as a mixture of two or more of them. A homogeneous, paste-like composition cannot be obtained, if the amount of the silicone oil is smaller than 10 parts by weight. The amount exceeding 1,000 parts by weight does not yield sufficient viscosity increasing capability. Thus, the amount of silicone oils should be in the range of 10-1,000 parts by weight for 100 parts by weight of the silicone polymer.

The paste-like silicone composition of the third invention thus obtained has a smooth and homogeneous cultivard appearance. If the shearing force is not applied or applied only insufficiently, the two components are not mingled together due to insufficient swelling of the polymer in the silicone oil, resulting in a nonhomogeneous product with no smoothness both in the outward appearance and in the sensation to the touch

A triple roll mill, double roll mill, sand grinder, colloid mill. Gaurin homogenizer, or the like can be used for the kneading under the shearing force. The use of a triple roll mill is especially preferable.

The water-in-oil type cosmetic composition of the fourth invention is characterized by incorporating said paste-like silicone composition in oil phase components. Although there are no limitations to the amount of the paste-like silicone composition to be incorporated, a preferable range is 10-90% by weight (hereinafter simply referred to as %) of the oil phase components.

Beside the paste-like silicone composition, oily materials conventionally used for cosmetic compositions can be incorporated as the oil phase components to the extent that they do not interfere the homogeneity of the oil phase. Such oily materials may be liquid oils, semi-solid oils, or solids oils, and can be used either singly or in combination of two or more of them. Given as examples of liquid and semi-solid oils are liquid paraffin, squalane, caster oil, isopropyl myristate, isopropyl palmitate, tanolin, petrolatum, olive oil, jojoba oil, macadamia nut oil, mink oil, turtle oil, almond oil, safflower oil, avocado oil, octyldodecyl myristate, cetyl 2-ethylhexanoate, fatty acid esters of glycerine (e.g., 2-ethylhexanoic triglyceride, isostearic diglyceride), fatty acid esters of propylene glycol (e.g., dicapriric propylene glycol) fatty acid esters of dipentaerythritol, oleic acid, oleyl alcohol, and the like.

As solid oils, hydrocarbons, waxes, hydrogenated oils, higher fatty acids, higher alcohols, and the like can be used. Specific examples include solid paraffin wax, ceresine wax, microcrystalline wax, carnauba wax, candelilla wax, bees wax, wood wax, whale wax, polyethylene wax, hydrogenated castor oil, rhodinic acid ester of pentaerythritol, stearic acid, lauric acid, myristic acid, behenic acid, cetyl alcohol, stearyl alcohol, lauryl alcohol, and the like.

Furthermore, an oil gelling agent may also be added to the oil phase in order to obtain a water-in-oil type cosmetic composition of solid or semi-solid type. Oil gelling agents which can be used include metal soaps, e.g., aluminum stearate, magnesium stearate, etc., fatty acid esters of polysaccharide, e.g., sucrose palmitate, starch palmitate, etc., montmorillonite clays, e.g., montmorillonite modified with dioctadecyl-dimethylammonium, montmorillonite modified with dihexadecyldimethylammonium, and the like.

The oil phase components are incorporated in the water-in-oil type cosmetic composition in an amount of 10-99%. If less than 10%, it is difficult to make the composition water-in-oil type; if more than 99%, the cosmetic composition is a very heavy to the touch.

The addition of silicic acid anhydride or hydrophobic silica to the oil phase components of the water-inoil type cosmetic composition, according to the fifth invention, remarkably promotes the stability while keeping the excellent sensation upon use of the paste-like silicone composition.

Silicic acid anhydride and hydrophobic silica used here may be those conventionally used in cosmetic compositions. Commercial products such as Aerosil 200. Aerosil 300 (trademarks, manufactured by Degussa Co.), or the like can be used as a suitable silicic acid anhydride. As hydrophobic silica, commercially available silicone-treated silica such as CAB-O-SIL TS-530 (trimethylsiloxylated silica: trademark, manufactured by Cabbot Co.), Aerosil R-972 (dimethylsiloxylated silica: trademark, manufactured by Degussa Co.), Aerosil R-805 (octylsiloxylated silica: trademark, manufactured by Degussa Co.), Aerosil R-202 (silicone oil treated silica: trademark, manufactured by Degussa Co.), and the like are commercially available and can be suitably used.

An effective amount of silicic acid anhydride or hydrophobic silica to be incorporated is in the range of 0.01-10% in the oil phase components. An amount exceeding 10% is undesirable, since the sensation of the product upon use is impaired and its stability is lowered

The water-in-oil type cosmetic composition of the present invention may contain, as water phase components, water as a main component and various water soluble components in an amount of 1-90%. If less than 1%, such an incorporation of water is effectively nil; if more than 90%, it is difficult to make the composition water-in-oil type. The addition of one or more components selected from the group consisting of sugars, sugar alcohols, and inorganic salts as water phase components remarkably improves the stability of the composition over time without the addition of silicic acid anhydride and hydrophobic silica (hereinafter referred to as the sixth invention).

Given as saccharides used here are monosaccharide, disaccharide, oligosaccharide, polysaccharide, such as glucoso fructoso, galactose, xylose, maltose, sucrose, lactose, starch, dextrin, and the like; as sugar aichnois sorbitol, mannitol, maltitol, and the like; and as inorganic salts, sodium, potassium, calcium, magnesium aluminum, or zinc salts of hydrochloric acid, surfunc acid, carbonic acid, nitric acid, or the like.

The effective amount of saccharides, sugar alcohols, and inorganic salts to be added is 0.1-20% of the total amount of the oil phase components. An amount exceeding 20% makes the resulting cosmetic composition sticky and impairs the sensation upon use.

Even though the water-in-oil type cosmetic composition of the present invention can disperse water easily therein without the addition of a surfactant, a low irritant nonionic surfactant may be incorporated in order to retain the water-in-oil system more stably. Preferable surfactants are polyoxyalkylene-modified organopolysiloxane typo surfactants (the seventh invention)

Polyoxyalkylene-modified organopolysiloxane type surfactants which can be used are those which are liquid or paste at normal temperature. Specific examples include compounds represented by the following formulas (4H6):

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wherein R^6 represents an alkyl group having 1-5 carbon atoms or a phenyl group, R^7 is a group $-(C_2P_4O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O)_{s^2}(C_3P_6O$

wherein R^c, R⁷, p and q are the same as defined in formula (4), R¹¹ is an alkyl group having 2-20 carbon atoms, R¹² and R¹³ are the same as at least one of R⁶, R⁷, and R¹¹, and u is a number of 1-30, provided that when q is 0, at least one of R¹² and R¹³ is the same as R⁷, and further that not all R⁶s can be phenyl group.

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wherein R14 represents an alkyl group having 1-4 carbon atoms, R15 is a group -Q1-O-(C2 H4 O)_X-(C3 H6 O)_X-(R15 (wherein Q1 is a hydrocarbon group having 1-4 carbon atoms, R15 is a hydrogen, an alkyl group having 1-4 carbon atoms, or an acetyl group, x is an integer of 1 or more, and y is an integer of 0 or more), R16 is a group -Q1-O-R25 (wherein Q2 is a hydrocarbon group having 1-4 carbon atoms and R20 is a hydrocarbon group having 8-30 carbon atoms), R17 and R18 are the same as: at least one of R14, R15, and R16, α is an integer of 0 or more, and β and γ are integers 1 or more.

Compounds represented by the above formula (4) are called polyether-modified silicone, exemplified by Silicon KF-945A (trademark, a product of Shin-etsu Chemical Co.), Silicon SH-3772C (trademark, a product of Toray-Dow Corning Silicone Co.), and the like

Compounds represented by the above formula (5) are called anytopyether-modified silicone, exemplified by Abit WE-09 (trademark, a product of Goldschumit Co) and the like.

Compounds represented by the above formula (6) are polycayalkylene alkyl ether-comodified organopolysiloxanes. They can be easily produced from methylhydrogenpolysiloxane by the co-modification with polycayalkylene alkyl ether and allylalkyl ether, for example, according to the method of Reference Examples described hereinafter.

Since these types of polyoxyalkylene-modified organopolysiloxane type surfactants possess good mutual solubility with the paste-like silicone composition in the oil phase, they can provide excellent stability.

These surfactants are preferably added to the cosmetic composition of the present invention in an amount of 0.01-10%, and particularly preferably 0.5-5%.

According to the eighth invention of the present application, various kinds of cosmetic powders can be incorporated into the water-in-oil type cosmetic composition of the fourth invention.

There are no specific limitations as to the cosmetic powders to be used. Body pigments, inorganic white pigments, inorganic colored pigments, organic pigments, organic powders, pearling agents, or the like can be used. Specific examples are tallous, kaolini, mica, magnesium carbonate, calcium carbonate, magnesium silicato, aluminum magnesium silicate, silica, titanium dioxide, zinc oxide, red iron oxide, yellow iron oxide, black iron oxide, ultramarine blue, tar pigment, nylon powder, polyethylene powder, polymethylmethacrylate powder, polystyrene powder, polytetrafluoroethylene powder, silk powder, crystalline cellulose, starch, titanated mica, iron oxide titanated mica, bismuth oxychloride, and the like.

These cosmetic powders may be used in an amount of 1-40%, and preferably 5-25%.

Preferred cosmetic compositions containing a cosmetic powder, which is the eighth invention, are those comprising the following components (a)-(e).

- (a) a semisolid oil or a liquid oil, or both,
- (b) a solid oil or an oil gelling agent, or both,
- (c) the above-mentioned paste-like silicone composition.
- (d) at least one water phase component, and
- (e) a cosmetic powder.

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The amount of the oil components (a) plus (b) is preferably 5-40%, and particularly preferably 15-30%, of the total amount of the cosmetic composition. Compositions containing an amount of oil components less than 5% does not function as an oily make-up cosmetic. If this amount is greater than 40%, the product is too oily, providing an impaired sensation upon use. Solid oils and oil gelling agents, the component (b), are preferably used in an amount of 5-50% in the total amount of the oil phase components and may be used either singly or in combination.

The amount of the paste-like silicone composition, the component (c), is preferably 5-60%, particularly preferably 15-40%. If this amount is smaller than 5%, the resulting cosmetic composition cannot stably hold large amounts of low viscosity silicone oils and water; if greater than 60%, the sensation upon use is impaired.

The amount of water, the component (d), is preferably 5-80%, and particularly preferably 10-60%, of the total amount of the cosmetic composition. If the amount of water is smaller than 5%, the waterish sensation upon use cannot be obtained; if greater than 80%, the stability over time is impaired.

Besides the above components, various components conventionally used for cosmetics can be optionally incorporated into the water-in-oil type cosmetic composition of the present invention to the extent that such incorporation does not impair the intended effects of the present invention. Such optional components include conventionally used aqueous components and oil components, e.g., moisturizers, preservatives, anti-oxidants, UV absorbers, skin-improvers, perfumes, water soluble polymer, tar colorants, and the like

The water-in-oil type cosmetic compositions of the present invention can be prepared by preparing the paste-like silicone composition in advance, and by mixing it with other components according to a conventional method.

The silicone polymer of the present invention can well swell in silicone oils and function as a good viscosity increasing agent for silicone oils. The paste-like silicone composition can disperse powders and pigments having specific gravities different from that of silicone oils, and can hold them therein in a stable manner without precipitating them. Therefore, the water-in-oil type cosmetic compositions in which this paste-like silicone composition in oil phase components is incorporated can well spread and provide a moistened sensation without stickiness. In addition, they are extremely stable over time.

Other features of the invention will become apparent in the course of the following description of the exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof

EXAMPLES

Synthetic Example

68 g of organohydrogenpolysiloxanes of which the average composition is shown by the compound of the following formula (7).

$$(CH3)3SiO = \begin{cases} CH3 \\ SiO \\ SiO \\ CH3 \end{cases} \begin{cases} H \\ SiO \\ SiO \\ CH3 \end{cases} Si(CH3)3$$
 (7)

100 g of othanol. 32 g of polyoxyalkylenes of which the average composition is shown by a compound of formula CH₂ = CHCH₂O(C₂H₄O)_{1c}CH₃, and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and stirred for 2 hours while keeping the internal temperature at 70-80 °C,

followed by evaporation of the solvent under reduced pressure to obtain organohydrogenpolysiloxanes of which the average composition is shown by the compound of the following formula (8).

$$(CH_3)_3SiO = \begin{bmatrix} CH_3 \\ 1 \\ SiO \end{bmatrix}_{24} = \begin{bmatrix} CH_2CH_2CH_2O(C_2H_4O)_{10}CH_3 \\ 1 \\ SiO \end{bmatrix}_{2} = \begin{bmatrix} H \\ 1 \\ SiO \end{bmatrix}_{2} Si(CH_3)_3$$

$$(8)$$

Example 1

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100.0 g of organohydrogenpolysiloxanes of which the average composition is shown by the compound of the above formula (8), 100.0 g of ethanol, 28.9 g of dimethylpolysiloxanes of which the both ends were sealed by dimethylvinylsilyl groups and of which the average composition is shown by the compound of the following formula (9).

$$\begin{array}{c|c}
CH_3 & CH_3 \\
CH_2 = CH - Si - O - Si O - Si - CH = CH_2 \\
CH_3 & CH_3 & CH_3
\end{array}$$
(9)

and 0.3 g of 3 who solution of chloroplatinic acid in otherol wore charged into a reaction vessel and stirred for 2 hours while keeping the internal temperature at 70-80°C, followed by evaporation of the solvent under reduced pressure to obtain an elastic silicone polymer. 20 parts by weight of this silicone polymer and 80 parts by weight of dimethylpolysiloxane (viscosity at 25°C; 6 cSt) were mixed and dispersed, and thoroughly kneuded by a triple roll mill under a shearing force to obtain a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 32,000 cP.

Fifty parts by weight of the paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

For comparison, the dispersod mixture with the same composition as above, 20 parts by weight of the silicone polymer, and 80 parts by weight of dimethylpolysioxane, was stirred for 2 hours at room temperature by a pranetary mixer instead of a triple roll mixer. The polymer did not swell homogeneously, fairing to produce a paste-like composition with a smooth sensation. Water added to the resulting mixture could hardly disperse, and oil and water were separated into two layers.

The above results demonstrate that only an application of a sufficient shearing force permits the silicone collymor of the present invention to swell and homogeneously disperse in a silicone oil, providing a paste-like silicone composition with an increased viscosity which gives a smooth sensation. Such a paste-like silicone composition cannot be produced under any conditions without a shearing force.

Example 2

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100.0 g of organohydrogenpolysiloxanes of which the average composition is shown by the compound of the following formula (10).

$$(CH_3)_3SiO = \begin{bmatrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{bmatrix}_{27} \begin{bmatrix} H \\ | \\ SiO \\ | \\ CH_3 \end{bmatrix}_{2}$$
 (10)

62.0 g of ethanol, 23.6 g of polyoxyalkylene of which the average composition is shown by the compound of the following formula (11).

$$CH_2 = CHCH_2O(C_2H_4O)_{10}CH_2CH = CH_2$$
 (11)

and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicone polymer particles.

33 parts by weight of this silicone polymer and 67 parts by weight of dimethylpolysiloxane (viscosity at 25°C: 6 cSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to obtain a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 24,800 cP. 50 parts by weight of this paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

5 Example 3

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100 g of organohydrogenpolysiloxanes of which the average composition is shown by the compound of formula (7) used in Synthetic Example, 75 g of ethanol, 49 4 g of polyoxyalkylenes of which the average composition is shown by the compound of formula (11) used in Example 2, and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicone polymer particles.

33 parts by weight of this silicone polymer and 67 parts by weight of dimethylpolysiloxane (viscosity at 25°C 6 cSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing to obtain a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 10,600 cP. 50 parts by weight of the paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a nomogeneous creamy composition.

Example 4

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100 g of organchydrogenpolysiloxanes of which the average composition is shown by the compound of the following formula (12),

$$(CH3)3SiO = \begin{bmatrix} CH3 \\ I \\ SiO \\ CH3 \end{bmatrix} = \begin{bmatrix} H \\ I \\ SiO \\ CH3 \end{bmatrix} = Si(CH3)3$$
(12)

57 g of ethanol, 13.5 g of polyoxyalkylenes of which the average composition is shown by the compound of formula (11) used in Example 2, and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicone polymer particles.

20 parts by weight of this silicone polymer and 80 parts by weight of dimethylpolysiloxane (viscosity at 25°C: 6 cSt) were mixed and dispersed, and thoroughly kneeded by a triple roll mill under a shearing force

to swell the silicone polymer, thus obtaining a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 22,800 cP. 50 parts by weight of the paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

Example 5

100.0 g of organohydrogenpolysiloxanes prepared in Synthetic Example, 58 g of ethanol, 17.7 g of polyoxyalkylene of the following formula (13),

$$CH_2 = CHCH_2 O(C_2 H_4 O)_8 (C_3 H_6 O)_2 CH_2 CH = CH_2$$
 (13)

and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicone polymer particles.

20 parts by weight of this silicone polymer and 80 parts by weight of dimethylpolysiloxane (viscosity at 25°C: 10 cSt) were mixed and dispersed, and thoroughly knoaded by a triple roll mill under a shearing force to swell the polymer, thus obtaining a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 15,000 cP. 50 parts by weight of the paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

Example 6

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100 g of organohydrogenpolysiloxanes of which the average composition is shown by the compound of the following formula (14).

76 g of ethanol 53 g of polyoxyalkyleno of which the average composition is shown by formula (11) used in Example 2, and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicone polymer particles.

30 parts by weight of this silicone polymer and 70 parts by weight of decamethylcyclopentasiloxane (viscosity at 25°C 2 cSt) were mixed and dispersed, and thoroughly knowed by a triple roll mill under a shearing force to swell the silicone polymer, thus obtaining a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 18,000 cP. 50 parts by weight of the paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

Example 7

100 g of organohydrogenpolysiloxanes of which the average composition is shown by formula (10) used in Example 2, 103.0 g of ethanol; 23.6 g of polyoxyalkylenes of which the average composition is shown by formula (11) used in Example 2, 82.4 g of dimethylpolysiloxane (viscosity at 25°C; 6 cSt), and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain a silicone polymer.

100 parts by weight of this silicone polymer and 100 parts by weight of dimethylpolysiloxane (viscosity at 25 °C. 6 cSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to swell the silicone polymer, thus obtaining a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 82,800 cP. 50 parts by weight of the paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

Example 8

100 g of organohydrogenpolysiloxanes of which the average composition is shown by formula (12) used in Example 4, 95.0 g of ethanol, 13.5 g of polyoxyalkylenes of which the average composition is shown by formula (11) used in Example 2, 75.7 g of dimethylpolysiloxane (viscosity at 25°C: 5 cSt), and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain a silicone polymer.

100 parts by weight of this silicone polymer and 200 parts by weight of octamethylcyclotetrasiloxane (viscosity at 25°C: 6 cSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to obtain a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 44,000 cP. 50 parts by weight of this paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

15 Example 9

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100 g of organohydrogenpolysiloxanes of which the average composition is shown by the compound of the following formula (15),

$$(CH3)3SiO = \begin{bmatrix} CH3 \\ SiO \\ SiO \\ CH3 \end{bmatrix}_{100} \begin{bmatrix} H \\ I \\ CH3 \end{bmatrix}_{2}$$
 (15)

74.0 g of ethanol, 18.5 g of polyoxyalkylenes of which the average composition is shown by the following formula (16)

$$CH_2 = CHCH_2 O(C_2H_4 O)_{3c} CH_2 CH = CH_2$$
 (16)

29 6 g cf dimethylpolysiloxane (viscosity at 25 °C; 6 cSt), and 0.3 g of 3 wt% solution of chloroplatinic acid in chanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicono polymer.

100 parts by weight of this silicone polymer and 200 parts by weight of phenyltris(trimethylsiloxy)silane were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to obtain a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 25 500 cP. 50 parts by weight of this paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stiming the mixture to give a homogeneous creamy composition.

Example 10

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100 g of organohydrogenpolysiloxanes of which the average composition is shown by formula (8) prepared in Synthetic Example, 72.0 g of ethanol, 28.9 g of dimethylpolysiloxane of which the both ends were sealed by dimethylpolysilyl groups and of which the average composition is shown by the compound of formula (9), used in Example 1, 14.3 g of dimethylpolysiloxane (viscosity at 25°C; 30 cSt), and 0.3 g of 3 with solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain a silicone polymer.

100 parts by weight of this silicone polymer and 350 parts by weight of dimethylpolysiloxane (viscosity at 25°C 6 cSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to obtain a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 48,000 cP. 50 parts by weight of this paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

Example 11

100 g of organohydrogenpolysiloxane prepared in Synthetic Example, 74 g of ethanol, 79 g of polyoxyalkylene of the following formula (17),

$$CH_2 = CHCH_2O(C_2H_4O)_5(C_3H_6O)_5CH_2CH = CH_2$$
 (17)

and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicone polymer particles.

100 parts by weight of this silicone polymer and 200 parts by weight of dimethylpolysiloxane (viscosity at 25 °C: 6 cSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to swell the polymer, thus obtaining a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 43,000 cP. 50 parts by weight of this paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

Example 12

100 g of organohydrogenpolysiloxane prepared in Synthetic Example, 72 g of ethanol, 28.9 g of organopolysiloxane of the following formula (18),

and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain silicone polymer particles.

100 parts by weight of this silicone polymer and 300 parts by weight of octamethyltrisiloxane (viscosity at 25°C, 1°CSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to swell the polymer, thus obtaining a silicone composition. This composition was a homogeneous paster-like material smooth to the touch and having a viscosity of 55,000 cP. 50 parts by weight of the paster-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

49 Example 13

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100 g of organohydrogenpolysiloxanes of which the average composition is shown by the compound of formula (10), used in Example 2, 103.0 g of ethanol, 23.6 g of polyoxyalkylene of which the average composition is shown by formula (11), used in Example 2, 82.4 g of 1.3-butylene glycol, and 0.3 g of 3 wt% solution of chloroptatric acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain a silicone polymer.

100 parts by weight of this silicone polymer and 100 parts by weight of dimethylpolysiloxane (viscosity at 25°C 50 cSt) were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing torce to swell the polymer, thus obtaining a silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 65,000 cP. 50 parts by weight of this paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

Example 14

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100 g of organohydrogenpolysilexane of which the average composition is shown by the compound of the following formula (19).

$$(CH3)3Sio = \begin{cases} CH3 \\ | \\ Sio \\ | \\ CH3 \end{cases} = \begin{cases} H \\ | \\ Sio \\ | \\ CH3 \end{cases} = Si(CH3)3$$
(19)

160 g of ethanol, 34.7 g of polyoxyalkylene of which the average composition is shown by the compound of the following formula (20).

$$CH_2 = CHCH_2O(C_2H_4O)_{3C}(C_3H_6O)_{1C}CH_2CH = CH_2$$
 (20)

20 g of ethylene glycol, 13.7 g of dimethylpolysiloxane (viscosity at 25°C: 10 cSt), and 0.3 g of 3 wt% solution of chloroplatinic acid in ethanol were charged into a reaction vessel and processed in the same manner as in Example 1 to obtain a silicone polymer.

100 parts by weight of this silicone polymer and 300 parts by weight of decamethylcyclopentasiloxane were mixed and dispersed, and thoroughly kneaded by a triple roll mill under a shearing force to obtain a swelled silicone composition. This composition was a homogeneous paste-like material, smooth to the touch and having a viscosity of 52,000 cP. 50 parts by weight of this paste-like silicone composition was mixed with 50 parts by weight of water. The water was easily dispersed by merely stirring the mixture to give a homogeneous creamy composition.

25 Reference Example 1

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183 g (0.1 mol) of methylhydrogenpolysiloxane of which the average composition is shown by the compound of the following formula (21),

$$\begin{array}{c|c}
CH_{3} & CH_{3} \\
CH_{3}-SiO & SiO \\
CH_{3} & CH_{3}
\end{array}$$

$$\begin{array}{c|c}
CH_{3} & CH_{3} \\
SiO & SiO \\
CH_{3} & CH_{3}
\end{array}$$

$$\begin{array}{c|c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$$

$$\begin{array}{c|c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$$

$$\begin{array}{c|c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$$

$$\begin{array}{c|c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$$

308 g (1 mol) of allyl oleyl ether, 136 g (0.3 mol) of allylated polyether of which the average composition is shown by the compound of the following formula (22).

$$CH_{2} = CHCH_{2}O(C_{2}H_{4}O)_{2}H$$
 (22)

and 500 g of ethanoi were weighed and placed in a 2 l flask. After the addition of 2 g of chloroplatinic acid neutralized with chlorine (an ethanol solution, platinum concentration: 0.5%), the mixture was reacted for 5 hours under refluxing of ethanol. After the reaction, the solvent was evaporated and nonvolatile materials were removed by filtration to obtain 570 g of oily product of organopolysiloxane comodified by polyoxyethylene oleyl ether, of which the average composition is shown by the compound of the following formula (23) (yield 91%)

Reference Example 2

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527 g of an oily product of organopolysiloxane comodified by polyoxyethylene and myristyl ether, of which the average composition is shown by the compound of the following formula (24), was prepared in the same manner as in Reference Example 1, except that 254 g (1 mol) of allyl myristyl ether was used instead of 308 g (1 mol) of allyl oleyl ether (yield: 92%).

Reference Example 3

610 g of an oily product of organopolysiloxane comodified by polyoxyothylene and isostearyl ether, of which the average composition is shown by the compound of the following formula (25) was prepared in the same manner as in Reference Example 1, except that 310 g (1 mol) of ally isostearyl ether was used instead of 308 g (1 mol) of allyl oleyl ether (yield: 97%).

Example 15 (Face Cream)

(Formulation)

	% by weight
(1) Paste-like silicone composition prepared in Example 4	10
(2) Octanoic triglyceride	30
(3) 1,3-Butylene glycol	20
(4) Purified water	Balance
(5) Perfume	q.s.

(Method of preparation)

- A. (1) and (2) were blended.
- B. (3) and (4) were blended.
- C. B was added to A while stirring and then (5) was added to the mixture.

A face cream obtained according to the above procedure could well spread and give a moistened sensation. It gave a fresh and excellent sensation upon use

Example 16 (Foundation)

(Formulation)

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% by weight 8.0 (1) Paste-like silicone composition prepared in Example 4 (2) Dimethylpolysiloxane (Viscosity at 25 °C: 6 cSt) 20 4.0 (3) Octanoic Triglyceride 6.0 (4) Diglycerol triisostearate 8.0 (5) Squalane (6) Methylphenylpolysiloxane 10.0 23.0 (7) Titanium dioxide 14.0 (8) Mica (9) Pigment -5.0 (10) Purified water Balance

(Method of preparation)

- A (1)-(6) were blended
- B (7)-(9) were blended and pulverized to homogenize
- C. B was added to A and the mixture was kneaded with a triple roll mill, followed by the addition of (10) while stirring.

The foundation obtained according to the above procedure gave a fresh sensation upon use without stickiness. It spread excellently over the skin producing a homogeneous cosmetic film and exhibiting superior make-up retentivity.

Examples 17-18, Comparative Example 1 (W/O Type Creams)

W O type croams with formulations shown in Table 1 were prepared according to the procedure outlined below. Their sensation upon use and stabilities over time were evaluated and rated according to the standard shown below. The results are shown in Table 1.

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TABLE 1

				% by weight
		<u>Exam</u> 17	<u>р 1 е</u> 18	Comparative Example 1
(1)	Paste-like silicone composition prepared in Example 4	10	10	10
(2)	Dimethylpolysiloxane (Viscosity at 25°C: 6 cSt)	5	5	5
(3)	Silicic acid anhydride (Aerosil 200)	0.2	-	-
(4)	Hydrophobic silica (CAB-O-SIL TS-530)	~	0.2	-
(5)	1,3-Butylene glycol	10	10	10
(6)	Ethanol	2	2	2
(7)	Preservative	q.s.	q.s.	q.s.
(8)	Purified water	Balance	Balance	Balance
Stab	oility over time (40°C)	_ · · · · · · · · · · · · · · · · · · ·		
	After 1 month	AAA	AAA	888
	After 3 months	AAA	AAA	B88
Fee l	ing upon use			
	Freshness	AAA	AAA	AAA
	Spreadability	AAA	AAA	AAA

(Method of preparation)

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- A (1)-(4) were blended
- 45 B (5)-(8) were heated and blended to homogenize.
 - C B was added to A while stirring and the mixture was cooled

(Evaluation standard)

50. Stability over time.

AAA Excellent with no change being observed

BBB Slightly gelled

CCC Slightly oozes liquid

DDD Oozes and separates liquid from solid

55 Feeling upon use

AAA Excellent

BBB. Good

CCC: Cannot ascertain good or bad

DDD: Bad

As can be seen from the above results, W/O type creams of Examples 17 and 18 exhibited superior stability over time, without losing the effects of the excellent sensation upon use provided by the paste-like silicone composition.

Example 19 (Creamy Eyeshadow)

(Formulation)

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	% by weight
(1) Paste-like silicone composition prepared in Example 13	10
(2) Dimethylpolysiloxane (Viscosity at 25 °C: 6 cSt)	10
(3) Octanoic triglyceride	20
(4) Hydrophobic silica (Aerosil R-972)	0.3
(5) Titanated mica	5
(6) Iron oxide titanated mica	5
(7) Mica	3
(8) Colored pigment	2
(9) 1,3-Butylene glycol	10
(10) Preservative	q.s.
(11) Perfume	q.s.
(12) Purified water	Balance

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(Method of preparation)

- A. (1)-(4) were blended and (5)-(8) were added to the blend to homogeneously disperse.
 - B (9), (10) and (12) were mixed and heated to dissolve.
 - C B was added to A and mixed with stirring, (11) was added to the mixture, and the whole mixture was cooled

Example 20 (Sunscreen Cream)

(Formulation)

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	% by weight
(1) Paste-like silicone composition prepared in Example 8	15
(2) Methylphenylpolysiloxane	5
(3) Cetyl 2-ethylhexanoate	5
(4) Hydrophobic silica (CAB-O-SIL TS-530)	0.5
(5) UV Absorber	5.5
(6) Pertume	q.s.
(7) 1,3-Butylene glycol	10
(8) Preservative	q.s.
(9) Purified water	Balance

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(Method of preparation)

- A. (3) and (5) were heated to dissolve, added to the mixture of (1), (2) and (4), and homogeneously blended.
 - B (7)-(9) were mixed and heated to dissolve.
 - C. B was added to A and mixed with stirring, (6) was then added, and the mixture was cooled.

The water-in-oil type cosmetic compositions prepared in Examples 19 and 20 exhibited an excellent sensation upon use which is superior to any conventional cosmetic compositions. They were fresh giving no sticky sensation and very stable over time.

5 Examples 21-24, Comparative Example 2 (W/O Type Creams)

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• W/O type creams with formulations shown in Table 2 were prepared according to the procedure cutlined below. Their sensation upon use and stabilities over time were evaluated and rated according to the standard shown below. The results are shown in Table 2.

50	45	25	30	20	15	10	5
		,	TABLE 2	2			
	Section 197					& by	% by weight
				Example	(e		
		,	(21)	(22)	(23)	(24)	Comparative Example 2
(1)	Paste-like silicone prepared in Example	Paste-like silicone composition prepared in Example 4	10	10	10	10	10
(2)	Dimethylpolysiloxane (Viscosity at 25°C: 6 cSt)	iloxane 25°C: 6 cSt)	S.	ĸ	S.	2	5
(3)	Octanoic triglyceride	lyceride	10	10	10	10	10
(4)	Glycerol		2	2	2	2	2
(3)	1,3-Butylene glycol	lycol	10	10	10	10	10
(9)	Maltose		2	•	,	2	ı
(7)	Sorbitol (70% aqueous solution)	olution)	ı	٧.	ı	ı	ı
(8)	Sodium chloride	9	ı	ı	1	1	•
(6)	Preservative		9.8.	g.s.	g.s.	q.s.	q.s.
(10)	(10) Purified water		Balance	Balance	Balance	Balance	Balance

...Continued...

45 25	35	3 0	25	20	10	5
		TABLE	TABLE 2 (Continued)	ıed)		
			Example	ple		
		(21)	(22)	(23)	(24)	Comparative Example 2
Stability over time (after 4 weeks	er 4 weeks)					
At 5°C		AAA	AAA	AAA	ANN	ввв
At room temperature		AAA	AAA	AAA	AAA	AAA
At 40°C		A.A	AAA	AAA	AAA	ввв
Feeling upon use						
Freshness		ввв	888	AAA	ввв	AAA
Moistened sensation		AAA	AAA	ввв	AAA	ввв
Spreadability		A.	AAA	W.	AAA	AAA

55 (Method of proparation)

A (1)-(3) were biended

B (4+(10) were heated and blended to homogenize

C. B was added to A while stirring and the mixture was cooled.

(Evaluation standard)

5 Stability over time (after 4 weeks):

AAA: Excellent with no change being observed

BBB: Slightly gelled CCC: Slightly oozes fiquid

DDD: Oozes and separates liquid

10 Feeling upon use

AAA: Excellent

BBB: Good CCC: Canno

Cannot ascertain good or bad

DDD: Bad

As can be seen from the above results, W/O type creams of Examples 21-24 exhibited superior stability over time, without losing the effects of the excellent sensation upon use provided by the paste-like silicone composition.

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Example 25 (Creamy Foundation)

(Formulation)

5			% by weight
	(1)	Paste-like silicone composition prepared in Example 8	15
10	(2)	Dimethylpolysiloxane (Viscosity at 25°C: 6 cSt)	5
	(3)	Decamethylcyclopentasiloxane	5
15			
	(4)	Octanoic triglyceride	8
20	(5)	Silicone-treated powder *	20
	(6)	Maltose	2
	(7)	Sodium sulfate	0.5
25	(8)	Preservative	q.s.
	(9)	Perfume	q.s.
30	(10)	Purified water	Balance

Composition of silicone-treated powder

35	Titanium dioxide	40%
-	Mica	29%
	Talc	20%
	Red iron oxide	2%
	Yellow iron oxide	6%
40	Black iron oxide	28
	Methylhydrogenpolysiloxane	1%

45 (Method of preparation)

- A (5) was added to (1)-(4) to homogeneously disperse in (1)-(4)
- B $(6\mu(8))$ and (10) were heated to dissolve.
- C. B was added to A and mixed with stirring, (9) was added to the mixture, and the resulting mixture was cooled.

Example 26 (Hand Cream)

(Formulation)

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% by weight
10
5
5
q.s.
20
10
5
2
1
q.s.
Balance

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(Method of preparation)

- A (1)-(3) were blended.
- B (5)-(11) were heated to dissolve.
- C B was added to A and mixed with stirring, (4) was added to the mixture, and the resulting mixture was cooled

Example 27 (Creamy Rouge)

(Formulation)

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	% by weight
(1) Paste-like silicone composition prepared in Example 13	8
(2) Octanoic triglyceride	3
(3) Dimethylpolysiloxane (Viscosity at 25 °C 6 cSt)	3
(4) Liquid paraffin	2
(5) Titanium dioxide	3
(6) Taic	1
(7) Titanated mica	3
(8) Red #226	0.2
(9) Yellow tron oxide	0.8
(10) Glycerol	5
(11) 1.3-Butylene glycol	10
(12) Starch	2
(13) Preservative	q.s.
(14) Perturne	q.s.
(15) Purified water	Balance

(Method of preparation)

- A. (1)-(4) were mixed and to the mixture was added a homogeneous blend of (5)-(9) to homogeneously disperso the latter into the former.
 - B (10)-(13) and (15) were heated to dissolve.

C. B was added to A and mixed with stirring, (14) was added to the mixture, and the resulting mixture was then cooled.

Water-in-oil type cosmetic compositions prepared in Examples 25-27 exhibited an excellent sensation upon use which has not been experienced with conventional cosmetic compositions. They were well spreadable giving a moistened sensation upon use and were very stable over time.

Examples 28-30, Comparative Example 3 (W/O Type Creams)

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W/O type creams with formulations shown in Table 3 were prepared according to the procedure outlined below. Their sensation upon use and stabilities over time were evaluated according to the standard shown below. In addition, their colors were observed and the diameter water drop in the systems were measured. The results are shown in Table 3.

5	% by weight	Owit terrace	Example 3	ŀ	29	ស	2	i	ı	0.3	1.2	5
10	a¥P ∣		30	6	9	19	1	ŧ	7	0.3	1.2	2
15	:	ple								0.3	1.2	
20		Example	29	6	9	19	1	2	1	0	-	5
25	E		28	6.	20	S	2	1	1	0.3	1.2	5
30	TABLE			composition 2	cSt)		Polyoxyalkylene-modified organopolysiloxane surfactant *1	Polyoxyalkylene-modified organopolysiloxane surfactant *2	d actant xample 1			
35					9	ceride	Polyoxyalkylene-modified organopolysiloxane surfa	Polyoxyalkylene-modified organopolysiloxane surfa	Polyoxyalkylene-modified organopolysiloxane surfactant prepared in Reference Example			ycol
•0				ke sili in Exa	polysil ty at 2	trigly:	lkylene lysilox	ılkylene olysilox	ilkylene olysilox i in Ref	icid	sitrate	lene gl
45				Paste-like silicone prepared in Example	Dimethylpolysiloxane (Viscosity at 25°C: 6	Octanoic triglyceride	Polyoxya organopo	Polyoxya organopo	Polyoxya organopc prepared	Citric acid	Sodium citrate	1,3-Butylene glycol
50				(1)	(2)	(3)	(4)	(5)	(9)	(7)	(8)	(6)

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... Continued ...

40 45	25	30	25	20	15	10	5
		TABLE	TABLE 3 (Continued)	(pənu			
				Example			
			28	29		30	comparative Example 3
(10) Preservative			d.s.	q.s.		q.s.	q.s.
(11) Perfume	•		.s.p	q.s.		q.s.	9.8.
(12) Purified water			Balance	Balance	Ba	Balance	Balance
Stability over time			AAA	AAA		AAA	AAA
Feeling upon use							
Freshness			AAA	AAA		ввв	ввв
Moistened sensation	tion		888	888		AAA	ວວວ
Smoothness upon	upon application	ر	AAA	AAA		AAA	ввв
Color			White	White		White	White
Diameter of water drops (µm)	rops (µm)		1-4	1-4		1-4	1-4
*1 A compound s=2-5, t=0	A compound of formula (4) with ${\rm R}^6 = {\rm R}^9 = {\rm CH}_3$, ${\rm R}^{10} = {\rm H}$, ${\rm p} = 20 - 30$, ${\rm q} = 2 - 5$, t=0	(4) with	R6=R8=R5	=CH3, R ¹⁰	сн, р	=20-30,	g=2-5, r=3,
*2 A compound group, p=20	A compound of formula (5) with $R^6=R^{12}=R^{13}=CH_3$, $R^{10}=H$, $R^{11}=C_{16}$ alkylgroup, p=20-60, q=1-10, r=3, s=2-10, t=2, u=2-20	(5) with $(r=3)$	R6=R12=F	13=CH3, R	10=H,	R ¹¹ =C ₁	6 alkyl

(Method of preparation)

A. (7). (8) and a portion of (12) were slowly added to a mixture of (4)-(8) with stirring to obtain a gel-like composition

B (1)-(3) were mixed. A was added to the mixture and heated to 70 °C

C (9), (10), and the remaining portion of (12) were mixed and heated to dissolve and kept at 70 °C.

D. C was added to B to emulsify, followed by the addition of (11), and the mixture was cooled to obtain a water-in-oil type cream.

(Evaluation standard)

Stability over time:

The composition was allowed to stand in a thermostat at 50°C to observe and evaluate the states of the compositions after 4 weeks.

AAA: Excellent with no change being observed

BBB: Slight separation was observed with formation of coagulation.

CCC: Separation was manifest with formation of coagulation.

Feeling upon use

DDD:

AAA: Excellent BBB: Good CCC: Average

Bad

As can be seen from the results of Table 3, creams prepared in Examples 28-30 were very stable and exhibited a good sensation upon use. They were fine emulsions when their colors were white. The cream of Comparative Example 3 in which no paste-like silicone composition was used formed the same as creams of the present invention, but exhibited insufficient stability over time and an unsatisfactory sensation upon use.

Example 31 (Creamy Foundation)

25 (Formulation)

		% by weight
30	(1) Paste-like silicone composition prepared in Example 7	8.0
	(2) Dimethylpolysiloxane (Viscosity at 25 °C; 6 cSt)	7.0
	(3) Octanoic trigtyceride	14.0
	(4) Dispositanoic acid neopentyl glycol	5.0
15	(5) Joroba oi!	2.0
	(6) Polyoxyalkylone-modified organopolysiloxane surfactant prepared in Reference Example 1	1.0
	(7) Titanium dioxide	8.0
	(8) Colored pigment	4.0
	(9) Mica	3.0
W	(10) Tarc	3.0
	(11) 1,3-Butylone glycol	4.8
	(12) Preservative	q.s.
	(13) Perturne	q.s.
	(14) Purified water	Balance

(Method of preparation)

- A (1)-(6) were mixed and (7)-(10) were added to the muxture to disperse homogeneously.
- B (11), (12) and (14) were heated to dissolve and added to A to emulsify. (13) was added to the resulting and the mixture was cooled.

The creamy foundations prepared by the above method were stable over time and provided an excellent sensation upon use giving a fresh sensation without stickiness. They have excellent water repellency and exhibited a high make-up effect.

Example 32, Comparative Examples 4 and 5 (Creamy Foundations)

Creamy foundations with formulations shown in Table 4 were prepared according to the procedure outlined below. Their sensation upon use and stabilities over time were evaluated and rated according to the standard shown below. The results are shown in Table 4.

TABLE 4 % by weight

	Example	% by weight Comparative Example		
	32	4	<u>se Example</u> 5	
(1) Starch fatty acid ester	2	2	4	
(2) Sucrose fatty acid ester	2	2	5	
(3) Octanoic triglyceride	6	6	21	
(4) Paste-like silicone composition prepared in Example 7	6	-	-	
(5) Silicone gel composition *1		6	10	
(6) Dimethylpolysiloxane (Viscosity at 25°C: 6 cSt)	9	9	25	
(7) Carboxy vinyl polymer	0.6	0.6	0.2	
(8) Sodium hydroxide	0.12	0.12	0.04	
(9) Purified water	Balance	Balance	Balanc	
(10) 1,3-Butylene glycol	. 5	5	5	
(11) Titanium dioxide	7	7	7	
(12) Inorganic pigment	1.8	1.8	1.8	
(13) Mica	0.8	0.8	0.8	
(14) Lecithin	0.2	- 0.2	0.2	
(15) Perfume	q.s.	q.s.	q.s.	
(16) Preservative	q.s.	q.s.	q.s.	
Stability	AAA	ccc	AAA	
Feeling upon use	AAA	-	BBB	

*1 Preparation of the silicone gel composition

^{1,790} g of dimethylhydrogenpolysiloxane of which the terminals were sealed by trimethylsilyl groups (average molecular weight: 2,340, Si-H 4.5 mol%) and 710 g of dimethylpolysiloxane of which the terminals

were sealed by dimethyvinyllsilyl groups (average molecular weight: 930, vinyl group 7.7 mol%) were charged into a planetary mixer with an internal volume of 5 I and stirred to mix. After the addition of 0.5 g of a 2% solution of chloroplatinic acid in isopropanol, the temperature was raised to 70-80 °C and the stirring was continued for 2 hours. The internal pressure was reduced to 5-10 mm Hg to perform stripping for 30 minutes, thus obtaining a partially crosslinked organopolysiloxane polymer as a colorless, flexible solid material.

100 parts by weight of dimethylpolysiloxane having a viscosity of 6 cS at 25 °C was dispersed in 100 parts by weight of this organopolysiloxane polymer and thoroughly kneaded to swell, thus obtaining a silicone gel composition.

(Method of preparation)

- A. (1)-(3) were mixed and heated to dissolve.
- B. (7)-(10) and (16) were mixed and dissolved.
- C. (11)-(15) were blended homogeneously and pulverized.
- D. (4)-(6) were mixed and B was added to the mixture.
- E. C and D were added to A and the mixture was homogenized to obtain a creamy foundation.

(Evaluation standard)

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Stability over time (after 4 weeks):

AAA: Excellent with no change being observed

BBB: Slight separation was observed

CCC: Separation was manifest

25 Sensation upon uso

AAA: clarifying and cool

BBB Not clarifying and cool, but refreshing

CCC: Sensation is oily with no refreshness

As can be seen from the results shown in Table 4, W'O type creamy foundation of Example 32 was very stable in spite of its high content of water and exhibited a fresh, clarifying and cool sensation which could not be afforded by conventional cosmetic compositions. In contrast, the foundation of Comparative Example 5, in which a silicone gel composition comprising a partially crosslinked organopolysiloxane polymer instead of the paste-like silicone composition of the present invention was used, provided no fresh, clarifying and cool sensation as exhibited by the foundation of the present invention, even though it was stable and gave a comparatively refreshing sensation without oikness or stickiness. The stability of was damaged and the product became unusable with an increase of the water amount (Comparative Example 4).

Obviously numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described heroin.

The features disclosed in the foregoing description and in the claims may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

Claims

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A silicone polymer prepared by the addition polymerization of the following components (I) and (II),
 (I) an organohydrogenpolysiloxane represented by the following formula (1),

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wherein R1 represents a substituted or unsubstituted alkyl, aryl, or aralkyl group having carbon atoms of 1-18, or a halogenated hydrocarbon group; R2 represents a group,

$$-C_nH_{2n}O(C_2H_4O)_{cl}(C_2H_4O)_{el}R^3$$
 (3)

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wherein R³ is a hydrogen, a saturated aliphatic hydrocarbon group having 1-10 carbon atoms, or a group -(CO)-R⁵ (wherein R⁵ is a saturated aliphatic hydrocarbon group having 1-5 carbon atoms), d is an integer of 2-200, and e is an integer of 0-200, provided that d + e is 3-200, and n is 2-6; a is a

value satisfying inequality $1.0 \le a \le 2.5$; b is a value satisfying inequality $0.001 \le b \le 1.0$; and c is a value satisfying inequality $0.001 \le c \le 1.0$; or an organohydrogenpolysiloxane represented by the following formula (2),

5 $R^1_1H_0SiO_{(4-1-0)/2}$ (2)

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wherein R¹ is the same as defined in formula (1), f is a value satisfying inequality $1.0 \le f \le 3.0$, g is a value satisfying inequality $0.001 \le g \le 1.5$; or a mixture of said organohydrogenpolysiloxanes of formulas (1) and (2), and

(II) a polyoxyalkylene represented by the following formula (A),

$$C_mH_{2m-1}O(C_2H_4O)_n(C_3H_6O)_iC_mH_{2m-1}$$
 (A)

wherein h is an integer of 2-200, i is an integer of 0-200, provided that h + i is 3-200, and m is 2-6, or an organopolysiloxane represented by the following formula (B).

$$R_{j}^{1}R_{k}^{4}SiO_{(4-j-k)/2}$$
 (B)

wherein R¹ is the same as defined in formula (1). R⁴ is a monovalent hydrocarbon group having an aliphatic unsaturated bond at the terminal thereof and containing 2-10 carbon atoms, j is a value satisfying inequality $1.0 \le j \le 3.0$, and k is a value satisfying inequality $0.001 \le k \le 1.5$, or a mixture of the polyoxyalkylene of formula (A) and the organopolysiloxane of formula (B), wherein at least one organopydrogenpolysiloxane of formula (1) or at least one polyoxyalkylene of formula (A) is contained as an essential component of the addition polymerization.

- The silicone polymer according to Claim 1, which is prepared by the addition polymerization of the organonydrogenpolysiloxane represented by formula (2) and the polyoxyalkylene represented by formula (A).
- The silicone polymer according to Claim 1, which is prepared by the addition polymerization of the
 organohydrogenpolysiloxane represented by formula (1) and the organopolysiloxane represented by
 formula (B)
- The silicone polymer according to Claim 1, which is prepared by the addition polymerization of the organohydrogenpolysiloxane represented by formula (1) and the polyoxyalkylene represented by formula (A)
 - A silicone polymer prepared by the addition polymenzation of 100 parts by weight of components comprising.
 - (I) an organohydrogonpolysiloxane represented by the following formula (1),

wherein R' represents substituted or unsubstituted alkyl, aryl, or aralkyl group having carbon atoms of 1-18, or a halogonated hydrocarbon group, R² represents a group $-C_nH_{2n}O(C_2H_4O)_d(C_3H_6O)_aR^3$, wherein R³ is a hydrogen, a saturated aliphatic hydrocarbon group having 1-10 carbon atoms, or a group $-(CO)-R^4$ (wherein R⁵ is a saturated aliphatic hydrocarbon group having 1-5 carbon atoms), d is an integer of 2-200, e is an integer of 0-200, provided that d + e is 2-200, and n is 2-6; a is a value satisfying inequality $1.0 \le a \le 2.5$; b is a value satisfying inequality $0.001 \le b \le 1.0$; and c is a value satisfying inequality $0.001 \le b \le 1.0$; and c is a value satisfying inequality $0.001 \le c \le 1.0$, or an organohydrogonpolysiloxane represented by the following formula (2).

wherein R' is the same as defined in formula (1), f is a value satisfying inequality 1.0 ≤ f ≤ 3.0, and g is a value satisfying inequality 0.001 ≤ g ≤ 1.5; or a mixture of said organohydrogenpolysiloxanes of formulas (1) and (2), and

- (II) a polyoxyalkylene represented by the following formula (A).
- $C_mH_{2m-1}O(C_2H_4O)_h(C_3H_6O)_iC_mH_{2m-1}$ (A)
- wherein h is an integer of 2-200, i is an integer of 0-200, provided that h + i is 2-200, and m is 2-6, or an organopolysiloxane represented by the following formula (B).
 - $R_i^*R_k^4SiO_{(4-j-k)/2}$ (B)
- wherein R¹ is the same as defined in formula (1). R⁴ is a monovalent hydrocarbon group having an aliphatic unsaturated bond at the terminal thereof and containing 2-10 carbon atoms, j is a value satisfying inequality 1.0 ≤ j ≤ 3.0, and k is a value satisfying inequality 0.001 ≤ k ≤ 1.5, or a mixture of the polyoxyalkylene of formula (A) and the organopolysiloxane of formula (B), wherein at least one organohydrogenpolysiloxane of formula (1) or at least one polyoxyalkylene of formula (A) are contained as an essential component of the addition polymerization, in the presence of 3-200 parts by weight of a low viscosity silicone oil having a viscosity of 100 cS or lower at 25 °C or a polynydric alcohol, or both.
- 6. The silicone polymer according to Claim 5, which is prepared by the addition polymerization of the organohydrogenpolysiloxane represented by formula (2) and the polyoxyalkylene represented by formula (A).
 - 7. The silicone polymer according to Claim 5, which is prepared by the addition polymerization of the organonydrogenpolysiloxane represented by formula (1) and the organopolysiloxane by formula (B).
 - 8. The silicone polymer according to Claim 5, which is prepared by the addition polymerization of the organohydrogenpolysiloxane represented by formula (1) and the polyoxyalkylene represented by formula (A).
- 9. A paste-like silicone composition which can disperse water and is prepared by kneading 100 parts by weight of the silicone polymer of Claim 1 or Claim 5 and 5-1,000 parts by weight of a silicone oil under a shearing force
- 10. A water-in-oil type cosmetic composition comprising the paste-like silicone composition of Claim 9 as an oil phase component and at least one water phase component.
 - 11. A water-in-oit type cosmetic composition comprising (i) the paste-like silicone composition of Claim 9 and (ii) silicic acid anhydrate or hydrophobic silical or both as oil phase components, and at least one water phase component.
- 12. A water-in-oil type cosmetic composition comprising the paste-like silicone composition of Claim 9 as an oil phase component and one or more components selected from the group consisting of sacchandes, sugar alcohols, and inorganic salts, as water phase components.
- 45 13. A water-in-oil type emulsion cosmetic composition comprising the paste-like silicone composition of Claim 9 as an oil phase component, at least one water phase component, and a polyoxyalkylenemodified organopolysiloxane type surface active agent
- 14. A water-in-oil type cosmetic composition comprising the paste-like silicone composition of Claim 9 as an oil phase component, at least one water phase component, and a cosmetic powder.
 - 15. A water-in-oil type make-up cosmetic composition comprising
 - (a) a semisolid oil or a liquid oil, or both,
 - (b) a solid oil or an oil gelling agent, or both,
 - (c) the paste-like silicone composition of Claim 9,
 - (d) at least one water phase component, and
 - (e) a cosmetic powder.

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Category	Citation of document with indication, w of relevant passages	here appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL5)
E	EP-A-0 501 791 (SHIN-ETSU LTD.) * claims 1-10 * * page 5, line 24 - page 8		1-10,14, 15	C08G77/46 A61K7/48 C08L83/12 //(C08L83/12,83:
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	* claims 1-5 * * page 5, line 24 - line 2 * page 5, line 37 - page 6 * page 6, line 52 - page 7 examples 1-4 *	, line 42 *		
	EP-A-0 420 253 (DOW CORNIN COMPANY, LIMITED) * claims * * page 2, line 26 - page 3	_	1,4	
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	<pre>page 2, line 30 ~ line 4 line 63 * page 3, line 14 - line 1</pre>		į	SEARCHED (Int. 0.5)
	* page 4, line 34 - page 5 * page 8, line 36 - line 3	, line 8 *		COBL A61K
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